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FTIR EVIDENCE FOR SURFACE AZIDES FORMED UPON AMMONIA ADSORPTION ON COPPER CATALYSTS

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The adsorption of ammonia on an alumina supported copper catalyst and on unsupported copper powder was studied by diffuse reflectance FTIR spectroscopy in the temperature range 423–643 K. Bands in the region between 1950 and 2350 cm^{-1} were identified as being due to surface-bound azides. These species are suggested to be possible precursors in the copper nitride formation observed earlier

1. Introduction

Alumina supported copper has been established as a highly selective catalyst for the amination of alcohols with ammonia and methyl amines [1]. The amination reaction is usually carried out in the presence of hydrogen. In the absence of hydrogen, severe catalyst deactivation due to the formation of surface copper nitride has been observed [2]. Copper nitride formation originates from reaction of the reactant amines with the copper surface, and is strongly suppressed in the presence of hydrogen [2–4]. It has been shown by surface enhanced Raman spectroscopy (SERS) that the nitrogen lone pair of the amine plays an important role in the precursor state of amine adsorption on copper surfaces [5], but relatively little is known about the fragmentation processes [1,6] in which the adsorbed amine is decomposed to form copper nitride.

Here we report FTIR evidence for surface bound azides which are generated upon adsorption of ammonia on copper/alumina catalysts. Surface azides are suggested to be precursors of copper nitride.

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2. Experimental

The apparatus used consists of a diffuse reflectance cell and an environmental chamber (Spectra-Tech) in an FTIR spectrometer (Perkin-Elmer, model 1710), which is connected to a personal computer (Nixdorf, model 386 AT) for data processing. The temperature in the environmental chamber could be controlled within ±2 K.

Nitrogen (Linde, 99.999%) as the carrier gas and the reactant ammonia (Linde, 99.98%) were used without further purification. The continuous flows of the gases were controlled by flow controllers from ROTA.

γ-alumina (Merck, > 99.9%), copper oxide (Fluka, puriss. p.a., > 99.0%) and an alumina-supported copper catalyst containing 68 wt% CuO, were used as samples. The preparation of the Cu/alumina catalyst is described in detail elsewhere [7]. The copper oxide sample and the copper/alumina catalyst were reduced by passing hydrogen (Linde, 99.999%) over the samples; the temperature was raised at a rate of 12 K/min and then held at 543 K for one hour. After this reduction treatment no H_2 uptake could be observed in subsequent TPR runs.

All spectra were recorded in diffuse reflectance with unpressed catalyst powders, which were pretreated by heating up to 623 K for 10 minutes under a continuous flow of nitrogen (12 l/h).

After setting the desired reaction temperature, the background spectrum was collected (200 scans at a resolution of 4 cm^{-1}). The ammonia was added ($NH_3 : N_2 = 1:10$ at a total flow rate of 11 l/h) and passed over the catalyst for 15 minutes. Subsequently the flow was switched to pure nitrogen, and the spectrum was recorded (50 scans, 4 cm^{-1}) and transferred to the computer. By this technique an adequate compensation of the temperature-dependent background was achieved.

In a second series of experiments γ-alumina and copper powder prepared by reduction of copper oxide in hydrogen were covered by a layer of sodium azide (Merck, > 99%). This layer was deposited by stirring the sample in a 10^{-3} mol/l solution of NaN_3 in ethanol for 30 minutes. After drying the sample at 373 K, the spectrum was recorded (200 scans, 4 cm^{-1}) and ratioed with the background, that had been collected with identical acquisition parameters on the pure catalyst (i.e., not impregnated with sodium azide).

3. Results and discussion

3.1. γ-Al_2O_3

When ammonia was adsorbed on γ-alumina, five bands were observed at temperatures up to 473 K (bottom trace in fig. 1). In agreement with the detailed analysis by Dunken and Fink [8], the two strong bands at 1220–1290 and 1635

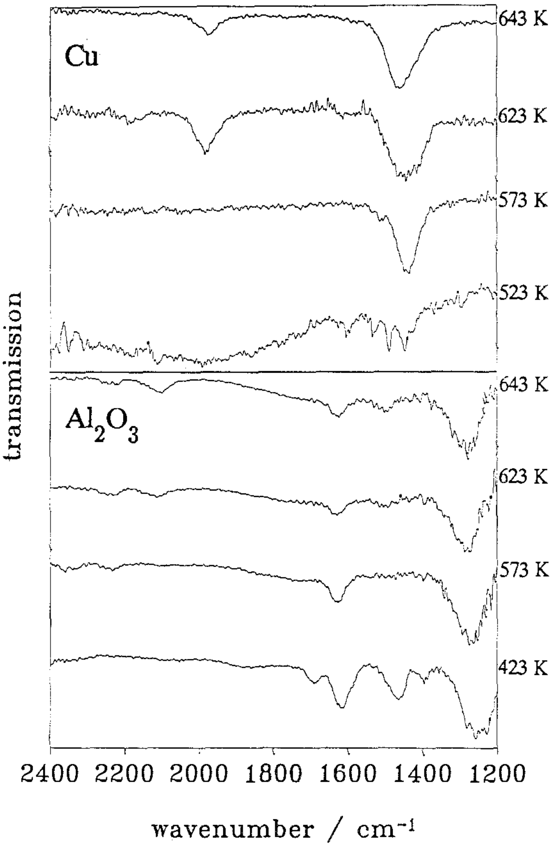

Fig. 1. Lower part: IR spectra recorded after adsorption of ammonia on γ-alumina at 423, 573, 623, and 643 K. Upper part: IR spectra recorded after adsorption of ammonia on copper powder at 523, 573, 623, and 643 K.

cm^{-1} were assigned to ammonia on Lewis-acid sites, and the absorptions at 1390, 1460–1500 and 1690 cm^{-1} to Brönsted-site bound ammonia.

The intensity of all peaks decreases when the temperature is raised. The absorptions assigned to Brönsted-sites decrease faster with increasing temperature and disappear at temperatures above 473 K (fig. 1). At temperatures above ~ 570 K three bands appear at 2115, 2240, and 2350 cm^{-1}. An assignment of these absorptions will be given in section 3.3.

3.2. COPPER

When ammonia was passed over the reduced CuO sample at room temperature, a weak pair of bands was detected at 1450 and 1495 cm^{-1}. These bands show strongly increasing intensity with raising temperature and merge into a single broad absorption extending from 1410 to 1500 cm^{-1} at 573 K (fig. 1). A very weak band at 1620 cm^{-1} is discernible at elevated temperatures. As mentioned in section 3.1, species adsorbed on Brönsted-sites would show a decreasing intensity with raising temperature and desorb completely at 523 K. Therefore the absorptions observed here can be assigned to strongly bound ammonia on positively charged centers. Oxidized copper atoms [Cu(II) and/or Cu(I)] that are persisting on the catalyst surface due to incomplete reduction of the CuO precursor, are likely adsorption sites. The presence of some unreduced copper is expected as water and oxygen traces have not been removed from the reactant gases. Dunken and Fink [8] have described this binding state as the "NH_3^+ limiting case of coordination", which is characterized by bands at 1500 and 1625 cm^{-1}. This assignment is in agreement with a recent study of ammonia and methylamine adsorption on copper/alumina [9]. — At temperatures above ~ 620 K, a band centered at 1980 cm^{-1} appears, which will be assigned in section 3.3.

3.3. BANDS IN THE FREQUENCY RANGE BETWEEN 1950 AND 2300 cm^{-1}

When ammonia is adsorbed on γ-alumina or on copper derived by reduction of CuO in hydrogen at elevated temperatures, absorptions are observed in the region between 1950 and 2400 cm^{-1}. Azides have been found to absorb in the same frequency range, e.g. NH_4N_3 and HgN_3 at 2041 and 2080 cm^{-1}, respectively [10]; CuN_3 shows two bands at 2000 and 2037 cm^{-1} [11]].

In the following, the adsorption of sodium azide on the substrates investigated in this study will be used to identify the bands in the 1950–2350 cm^{-1} region. For reference, the spectrum of bulk sodium azide diluted with KBr is discussed first. In the bottom trace of fig. 2, at least six significant bands are discerned in the range between 1900 and 2300 cm^{-1}, all of which correspond to the asymmetric stretching motion (ν_3) of the $N=N=N^-$ group in various local environments. While obviously there is only one such vibration in solution, the 'correlation splitting' [10] (factor group splitting) in the solid gives rise to several bands in this frequency range. Vibrations at 2043, 2128, 2160, and 2189 cm^{-1} are reported in ref. [10], all of which are observed in the bottom spectrum of fig. 2.

To proceed further in the interpretation, it is interesting to compare the ν_3 frequencies of azide with various counterions [11]. For HN_3, a frequency of 2140 cm^{-1} is reported, whereas with K^+ as the counterion, ν_3 is observed at 2036 cm^{-1} [11]. When we investigate thin azide layers on the catalyst substrates, we expect to observe one or several surface species, with frequencies that depend on the interaction between the azide ion and the substrate.

As described in the experimental section, layers of sodium azide were coated onto the catalysts, to confirm our assignment of the bands observed in the 1950–2350 cm^{-1} region to surface-bound azides. Spectra collected after covering the catalysts with NaN_3 are compared in fig. 2 with spectra recorded after ammonia was passed over the samples at high temperatures. A layer of azide on

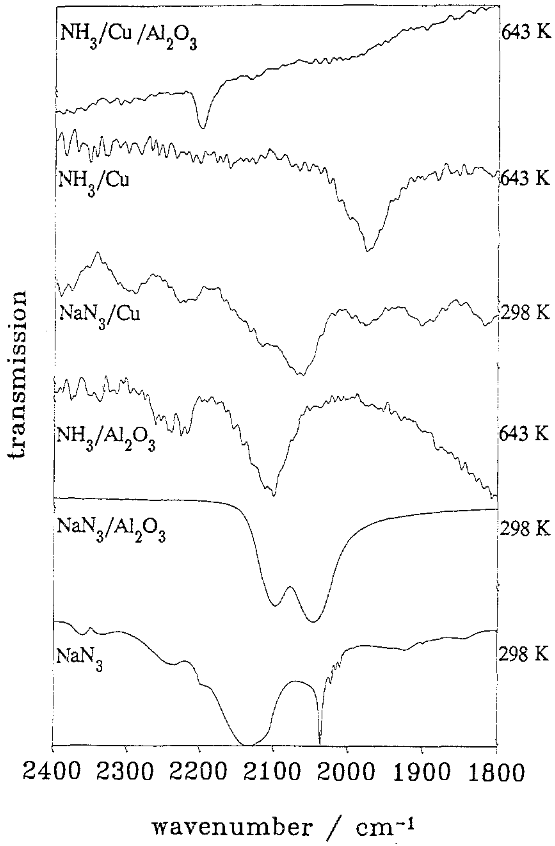

Fig. 2. Comparison of the IR absorptions observed on alumina and copper catalysts in the frequency region around 2000 cm^{-1}, with the spectra of sodium azide adsorbed on various surfaces. From bottom to top, the following systems are represented: a) NaN_3 : KBr = 1 : 1000 (wt%) at 298 K; b) NaN_3 on Al_2O_3 at 298 K; c) NH_3 adsorption on Al_2O_3 at 643 K; d) NaN_3 on copper powder at 298 K; e) NH_3 adsorption on copper powder at 643 K; f) NH_3 adsorption on Cu/alumina catalyst at 643 K.

alumina yields two peaks at 2035–2060 and 2095–2110 cm^{-1}. The spectrum of the corresponding NH_3 adsorption experiment at 643 K shows a matching band at 2070–2120 cm^{-1}, and a second absorption at 2220–2260 cm^{-1} which has a counterpart in bulk NaN_3 (fig. 2, bottom).

Sodium azide on copper exhibits an absorption at 2060–2080 cm^{-1} with a weak shoulder at 2120 cm^{-1}. The reaction of ammonia with copper at 643 K shows only one peak at 1975 cm^{-1}. This frequency is somewhat lower than the one observed at 2000 cm^{-1} in CuN_3. One might argue that on the electron rich copper surface, the $N=N=N^-$ stretching force constant is lower than in the ionic compound $Cu(I)N_3$.

In previous work [9], three to four bands were observed between 2000 and 2240 cm^{-1} when ammonia was adsorbed on a copper/alumina catalyst at temperatures above ~ 440 K. The spectra of the corresponding adsorption experiment in this study were recorded at a somewhat higher temperature (643 K). We observe a strong band at 2210 cm^{-1} and a weak and very broad absorption at 1950–2050 cm^{-1} (top trace in fig. 2).

Some alternative assignments of the bands observed on the catalysts will now be discussed. In the considered frequency range only few possible absorbing species are known [12,13]. Dunn et al. [14] have observed a band at 2056 cm^{-1} when passing NH_3 over polycrystalline platinum, and have assigned it to surface cyanide formed from carbon-containing impurities. To investigate this possibility, KCN has been adsorbed on the Cu/Al_2O_3 surface. A single band was observed at 2100 cm^{-1}; this frequency does not match the bands observed when passing NH_3 over Cu and Cu/Al_2O_3 (fig. 2). The only plausible source of carbon in our system would be trace CO impurities in the NH_3 reactant gas. Generally, gas phase CO is very sensitively detected in the environmental chamber used in our experiment. As we do not observe any trace of gaseous CO, the assignment of the bands to surface cyanides appears very unlikely. For the same reason, the formation of isocyanates, which was observed in ref. [15] upon passing stoichiometric amounts of CO and NH_3 over preoxidized Ru/Al_2O_3, can be excluded. From the described measurements and the comparison with the azide-impregnated catalysts, the absorptions observed in the frequency range between 1950 and 2350 cm^{-1} can therefore be confidently assigned to surface-bound azide species.

In earlier investigations [2,4] nitride formation was observed under similar conditions as the major route for catalyst deactivation, as mentioned above. It is interesting to discuss a possible role of surface azides in the mechanism of the catalyst deactivation. As shown in fig. 3, one could imagine a reaction pathway for the formation of these bulk nitrides with surface azide acting as a precursor. However, from the present data we can not discern whether azide is a precursor

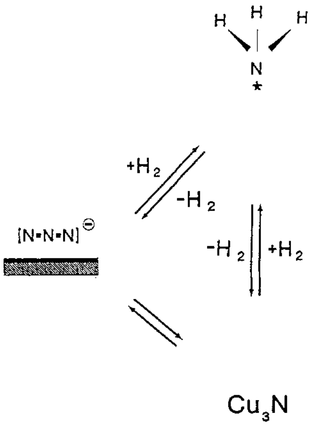

Fig. 3. Possible reactions of ammonia on copper containing catalysts in the absence of hydrogen.

of nitride, or whether the formation of the molecular N_3^- species is a side reaction occurring besides the nitride formation discussed above.

4. Conclusions

The adsorption of ammonia on γ-alumina and copper was investigated with FTIR spectroscopy. The absorptions observed on copper in the 1410–1500 cm^{-1} range have been assigned to ammonia molecules strongly bound at Lewis-acid sites, which are probably related to the presence of some unreduced CuO on the copper surface. These bands appear in the same frequency range as the absorptions of NH_3 adsorbed to Brönsted-sites on Al_2O_3. This fact explains the absence of new bands for NH_3 on Cu/Al_2O_3 in comparison to pure γ-alumina [11].

The bands in the region between 1950 and 2400 cm^{-1} were identified as being due to surface-bound azides. Surface azide species are observed prior to the formation of copper nitride, which occurs when ammonia interacts with copper in the absence of hydrogen at elevated temperatures.

Acknowledgments

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